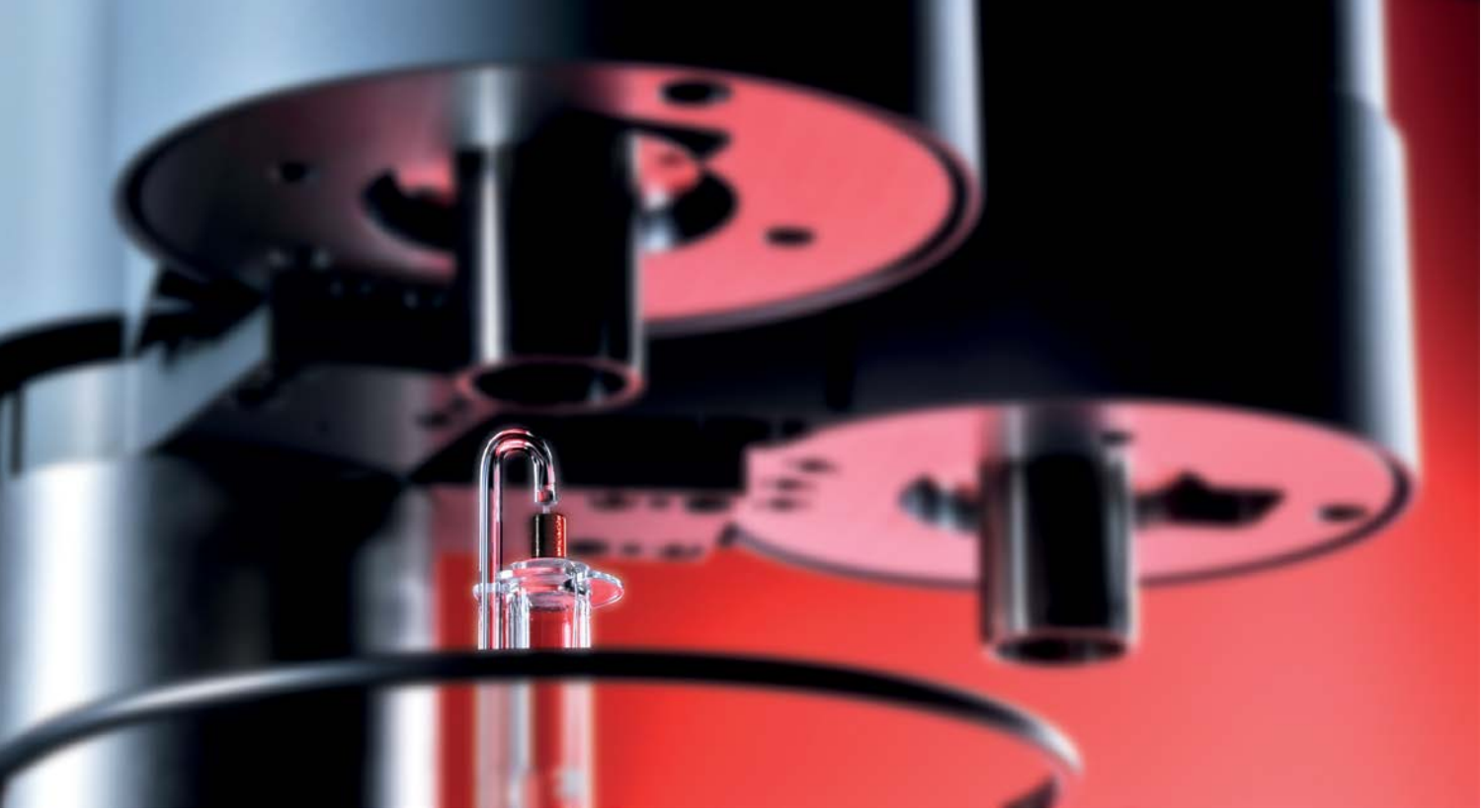
NETZSCH

Proven Excellence.

TMA 402 ***F1/F3*** *Hyperion®*

Thermomechanical Analysis – TMA
Method, Technique and Applications

Analyzing & Testing



Thermomechanical Analysis (TMA)

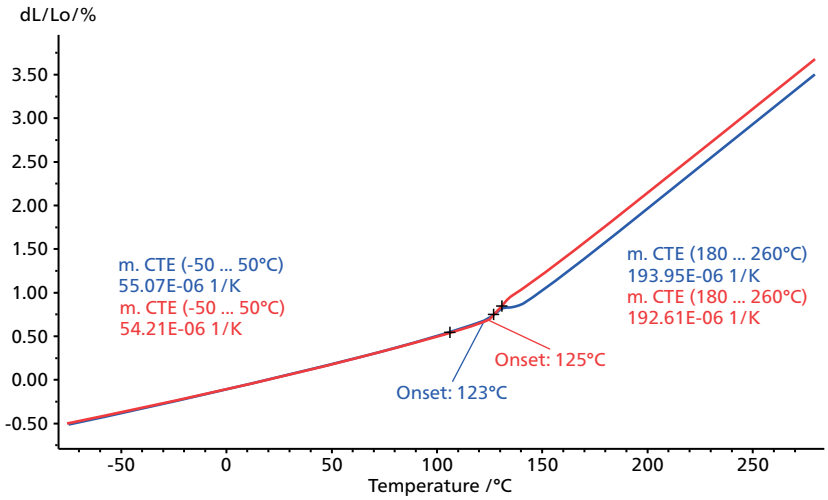
TMA Analysis Results

- Linear thermal expansion
- Coefficient of thermal expansion
- Phase transition temperatures
- Sintering temperatures
- Shrinkage steps
- Glass transition temperatures
- Dilatometric softening points
- Volumetric expansion
- Density changes
- Delamination
- Decomposition temperature
- Sintering kinetics
- Isostrain
- Creep
- Relaxation
- Stress/strain curve

Thermomechanical analysis (TMA) is a technique for determining the dimensional changes in solids, liquids or pasty materials as a function of temperature and/or time under a defined mechanical force (DIN 51005, ASTM E 831, ASTM D696, ASTM D3386, ISO 11359 – Parts 1 to 3). It is closely related to dilatometry, which determines the length change of samples under negligible load (DIN 51045).

Many materials undergo changes in their thermomechanical properties during heating or cooling. For example, phase changes, sintering steps or softening can occur in addition to thermal expansion. TMA analyses provide valuable insight into the composition, structure, production conditions and application possibilities for various materials.

Instruments for thermomechanical analysis are applied all the way from research and development to quality control. Typical domains include plastics and elastomers, thermosets, composite materials, adhesives, films and fibers, ceramics, glass and metals.



Measurement on an epoxy resin with a sample length of 6 mm in expansion mode (fused silica sample holder); 1st and 2nd heating runs at a rate of 2 K/min

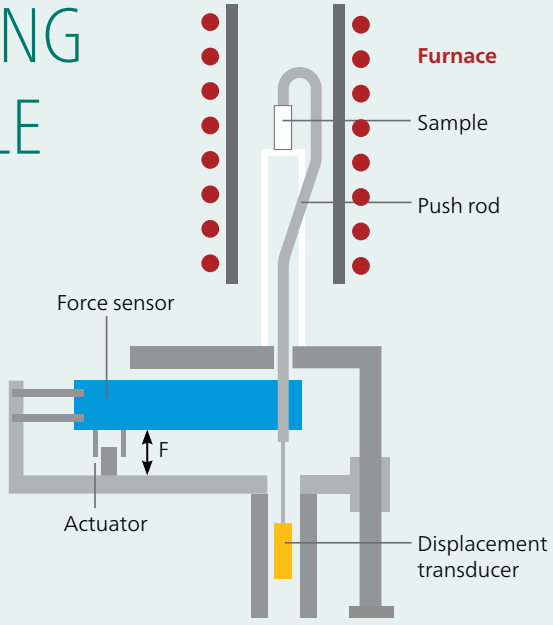
Thermal Expansion

The linear thermal expansion is an important variable for assessing the dimensional behavior of a material in response to a change in temperature.

This plot shows the thermal expansion (dL/L_0 in %) of an epoxy resin between -70°C and 270°C. In the first heating (blue curve), the onset of the glass transition (T_g) occurs at 123°C. In the second heating (red curve), the onset of T_g is slightly shifted, to 125°C. This shift could be due to relaxation effects or post-curing.

TMA MEASURES LENGTH CHANGES IN SOLIDS, POWDERS, PASTY MATERIALS AND LIQUIDS WITH PRECISION

OPERATING PRINCIPLE



Irrespective of the type of deformation selected (expansion, compression, penetration, tension or bending), every length change in the sample is communicated to a highly sensitive inductive displacement transducer (LVDT) via a pushrod and transformed into a digital signal.

The pushrod and corresponding sample holders of fused silica or aluminum oxide can be quickly and easily changed out, in order tooptimize the system for the respective application.

Thermomechanical Analysis

A Fundamental Analysis Technique For Material Properties

Detects Even the Slightest Dimensional Changes

The LVDT constitutes the centerpiece of the NETZSCH TMA 402 ***F1/F3*** *Hyperion*®. The technology behind it is tried-and-true: Even the slightest of length changes, into the nanometer range (digital resolution of 0.125 nm), can be measured and detected.

A variation of furnace options for all applications

To adjust the instrument for various temperature ranges and varied atmospheres, all that needs to be done is to change the furnace. This can be carried out by the operator. Thanks to the double furnace hoist, switching to a second furnace only takes moments.

Flexible Atmospheres in a Vacuum-Tight TMA System

All joints are designed to be vacuum-tight, allowing for measurements in a highly pure atmosphere or under vacuum. Mass flow controllers (MFCs) allow the use for up to 4 different gases and provide optimum control for purge and protective gases (optional for TMA 402 ***F3*** *Hyperion*®).

Made by NETZSCH in Germany

Simultaneous Measurement of Force and Displacement Signal

The force operating on the sample is generated electromagnetically. This ensures a quick response time for experiments with a changing load. A highly sensitive force sensor (digital resolution < 0.01 mN, max. force ±4 N) continuously measures the force exerted via the pushrod and readjusts it automatically. This sets the NETZSCH TMA 402 ***F1/F3*** *Hyperion*® apart from other instruments which only use preset values.

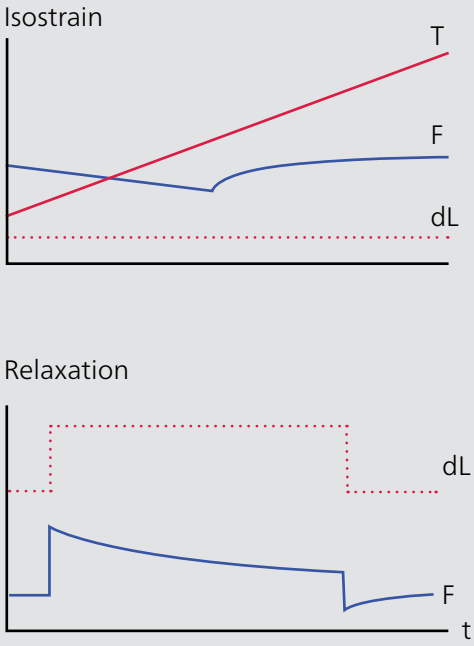
From Sensitive to Stiff Materials

The electronic control system allows users to set the force value in the mN-range. This enables testing even on sensitive materials such as thin fibers or films. For bigger geometries a force load up to 4 N can be applied using the premium TMA 402 ***F1*** *Hyperion*®model. The force being exerted upon the sample can be altered via the software in a stepwise or linear fashion. This makes it especially simple to carry out tests such as creep.

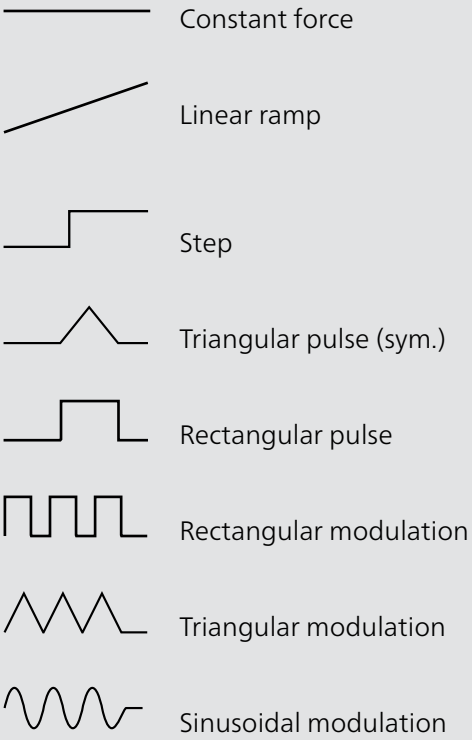
Determination of Visco-Elastic Properties like Relaxation, Creep and Stress/Strain

The TMA 402 ***F1/F3*** *Hyperion*® now offers not only the ability to keep the force constant and to measure the length change, but also to change the dL displacement and measure the corresponding force. This can, for example, be used in a stress relaxation test where a sample is stretched by a specific amount at a defined temperature. During the test, the deformation is kept constant and the progression of the force is recorded. This force continuously decreases as a result of material relaxation. The stress-relaxation is ultimately defined by the residual stress measured after a defined exposure period. The data can be depicted graphically in a stress-time diagram. It is then possible to read off both the stress-relaxation behavior and the values for the relaxation rate and time.

Displacement control



Force control



Highest Flexibility at Maximum Precision

The modular design of the TMA 402 ***F1/F3*** *Hyperion*® makes it unique among the competition. You are always prepared for the future!

One Instrument – Different Temperature Ranges

-150°C to 1000°C	Steel furnace with LN_2[1] cooling
-70°C to 450°C	IC-furnace with mechanical cooling without the need of LN_2[1]
RT to 1550°C	SiC furnace
-150°C to 500°C	Copper furnace, allows for measurements under controlled humidity environment from 0°C to 100°C
RT°C to 1250°C	Water-vapour furnace connected to a water-vapour generator

[1]LN_2 liquid nitrogen cooling

Interested in the gases evolving during thermal treatment?

The TMA 402 *F1/F3* Hyperion® can also be coupled to a mass spectrometer and/or FT-IR spectrometer.

Interchangeable Furnaces and Sample Thermocouples Provide Flexibility at Any Time

The TMA 402 ***F1/F3*** *Hyperion*® can thus cover the entire temperature range from -150°C to 1550°C. Within this range, the sample thermocouples available (type K and S) can be changed out quickly and easily. The system electronics recognize the installed sensor automatically.

Furnaces can be easily interchanged among various NETZSCH high-temperature thermal analysis instruments (e.g., STA 449 ***F1/F3*** *Jupiter*®, DSC 404 ***F1/F3*** *Pegasus*®).

Prepared for Future Applications – Large Variety of Easy Exchangeable Sample Holders

Depending upon the question at hand and the geometry of the sample, the operator has a variety of sample holders to choose from.

Holding devices for expansion, penetration, and tension measurements are available, as well as pushrods and supports for analyses in 3-point bending. Accessories for the temperature range up to 1100°C are made of fused silica. For the high-temperature range, aluminum oxide varieties are available.

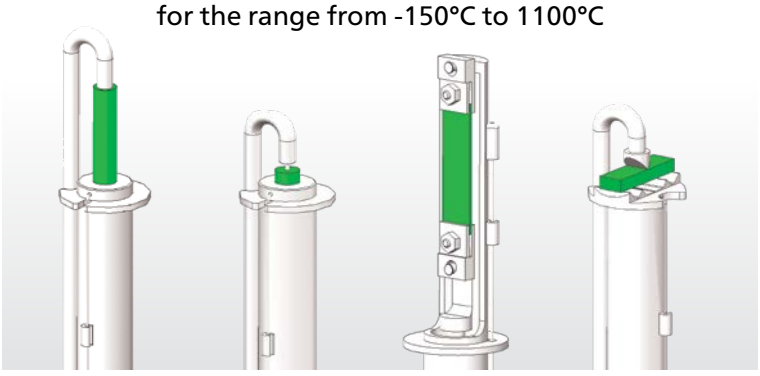
Not the Usual Sample?

With the help of special sample containers, the expansion behavior of powders, pastes and liquids can be analyzed, as can metals all the way to the melting point. Accessories for experiments on swelling behavior upon immersion are also available.

Measuring Modes and Sample Holders

Sample Holders for Copper, Steel, Water Vapor and SiC Furnce

Sample holders made of fused silica for the range from -150°C to 1100°C



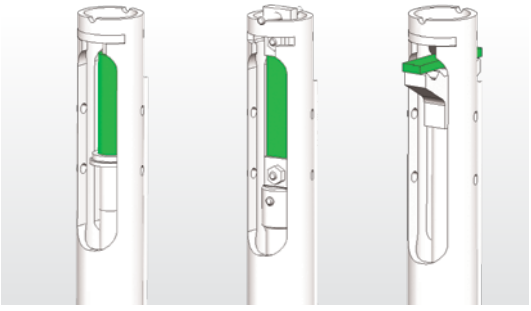
Expansion/ compression – pushrod with flat tip, Ø 4 mm

Penetration – pushrod with flat tip, Ø 1 mm

Tension, max. tension length 30 mm

3-point bending for free bending lengths 10 mm and 20 mm

Sample holders made of alumina for the range from RT to 1550°C



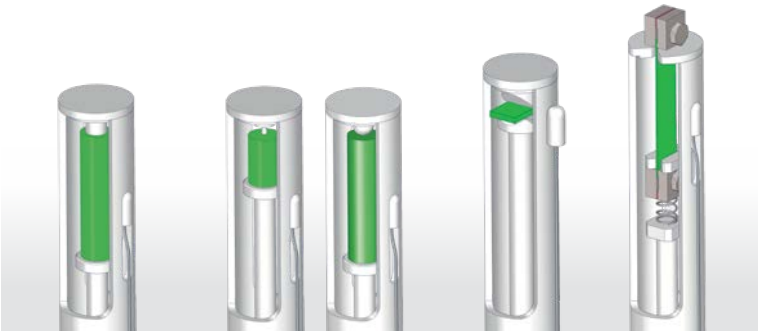
Expansion/ Penetration

Tension, max. tension length 30 mm

3-point bending, for free bending lengths 10 mm and 20 mm

Sample Holders Made of Fused Silica for IC Furnace*

*can be combined with other TMA furnaces



Expansion/ compression – sample holder tube with flat tip, Ø 4 mm

Penetration – sample holder tube with flat tip, Ø 1 mm (left) and hemispherical tip (right)

3-point bending, free bending length 5 mm

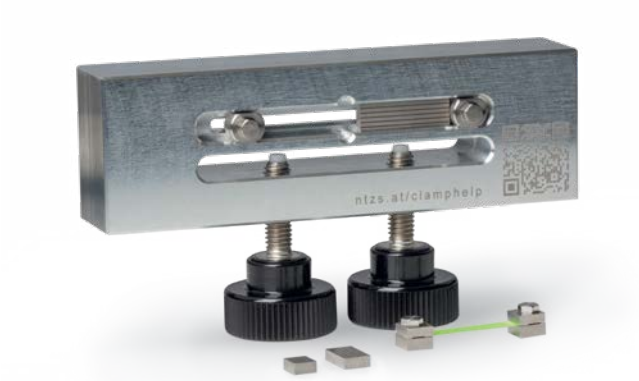
Tension, max. sample length 30 mm, min. 5 mm

From Bending to Tension – From Cylindrical Samples to Thin Films

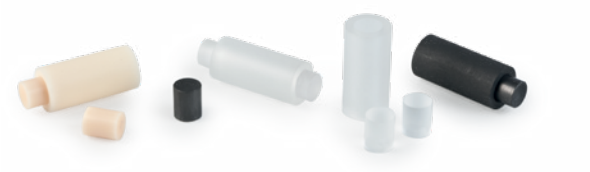
The **expansion/penetration** mode is used for samples with different geometries, such as cylindrical or rectangular. Sample fixtures are available in several tip diameters and shapes.

3-point bending can be used in two different bending lengths (10 mm and 20 mm). This allows for measurements on samples of varying sizes without having to change the sample holder.

The **tension** mode is used to measure expansion,shrinkage or relaxation on thin films or fibers. Very thin and sensitive samples can be prepared using the especially developped alignment fixture.



Alignment tool for sample preparation for measurements in tension mode



Sample Containers of alumina, sapphire and graphite for measurements on powders, pastes and liquids

Measurements in Humid Atmosphere

Simulation of Environmental Influences

For TMA measurements in humid atmospheres, there are two furnaces available.

The **water-vapor** furnace covers a temperature range from room temperature to 1250°C. The furnace can be connected to a humidity generator or to a water-vapor generator which produces steam by evaporating water.

The **copper** furnace can be used for conventional TMA measurements from -150°C to 500°C. It can be conveniently connected to a humidity generator, allowing for in-situ drying up to 500°C and a controlled humidity environment between 0°C and 100° C. For your convenience, a humidity calculator is integrated into the TMA *Proteus*® software.

Humidity Generator

Copper or Water-Vapor Furnace

- Defined relative humidity by mixing wet and dry gas flow
- Maximum dew point of 80°C, corresponding to 47% molar concentration
- Minimum 5% relative humidity at 20°C, corresponding to 0.1% molar concentration (or dry)
- Programmable humidity ramps/steps
- Easy refill, also while operating

Water-Vapor Generator

Water-Vapor Furnace

- Steam by evaporating liquid water
- Maximum 100% molar concentration
- Possible dilution by inert gas
- Minimum 5% molar concentration (or dry)
- Gas-tight tank

Water-vapor generator

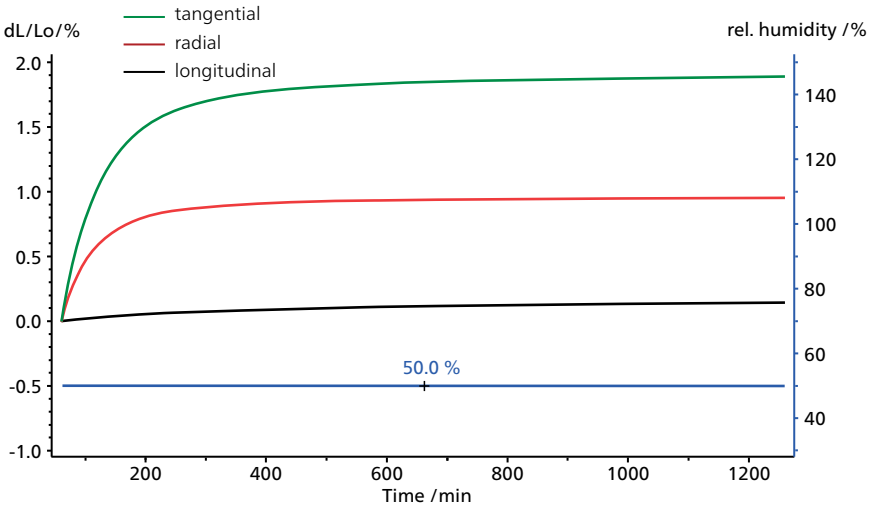
Humidity generator connected to TMA 402 ***F1*** *Hyperion*® with water-vapor furnace

Swelling Behavior of Wood Under Humid Conditions

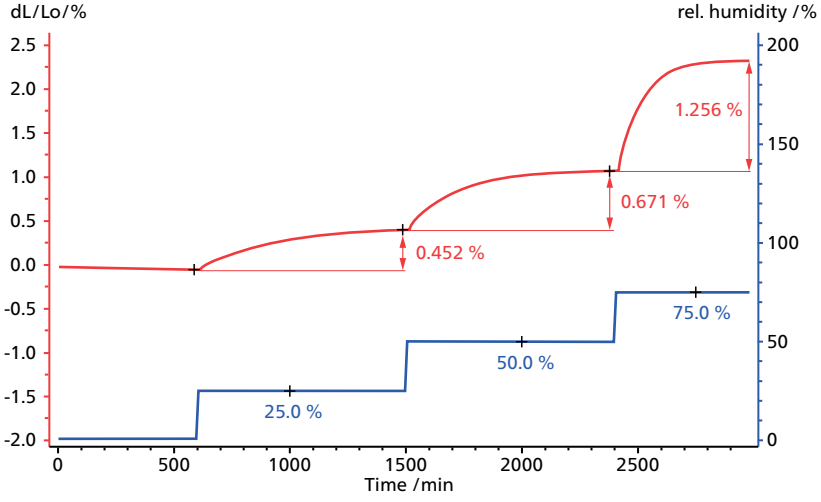
In the hygroscopic wood moisture range, the dimensions and the volume undergo change when moisture is absorbed by swelling and when moisture is released by shrinkage. For the practical use of wood, the following are particularly important:

- The dimensions of dry wood in the three anatomical directions when the ambient climate changes (differential swelling, swelling coefficient).
- The shrinkage of wood when drying from the wet (fresh) to the normal condition (drying rate).

To test the swelling behavior on beech wood, three samples were cut from the beech in tangential, radial and longitudinal directions (see picture sampling points). This plot shows the different expansion behavior of the three wood grain directions under 50% relative humidity at 25°C.



TMA with the copper furnace and humidity generator; sample holder made of fused silica; sample length 25 mm, cross-section 5 x 5 mm²



Isothermal measurement at 40°C with copper furnace and humidity generator; sample dimensions: length 15 mm x width 5 mm x thickness 0.25 mm

Hygroscopic Behavior of Polyamide

Depending on the relative humidity, dry PA 6 can absorb moisture from its environment and undergo thermal expansion of up to 10%. Such moisture absorbance can be simulated with TMA.

This plot shows the hygroscopic behavior of PA 6 film at 40°C in tension mode (sample holder made of fused silica). The relative humidity was increased from 0% to 75% in steps of 25% every 15 h. Over the course of 150 h, the total thermal expansion amounted to 2.4%.

Proteus® Software

Clever Features for Intelligent Analysis

Automatic determination of initial sample length in expansion, penetration and tension modes!

At a Glance – Highlights of the TMA *Proteus*® Software

TMA 402 *Hyperion*®	***F1***	***F3***
Automatic sample length detection	■	■
Force adjustment/ segment	■	■
Softening point detection	■	■
Density determination	■	□
c-*DTA*®	■	□
Force modulation	■	□
Temperature modulation	□	□
RCS	□	□
Strain control	■	■
Report generator	■	■
Identify	■	□
AutoEvaluation	■	■

■ Included in standard configuration
□ Optional

Identify – Identification and Classification of TMA Curves

The *Identify* database offers a state-of-the-art means of verifying materials; it allows for the comparison of a given curve to other individual curves (e.g., groups of curves in quality control) or to literature data from selected libraries. Any libraries and classes created by the user can be edited or expanded within *Identify*.

The standard libraries – comprising over 1100 entries – include measurements and literature data for DSC, c_p, TGA, and DIL/TMA from the application fields of polymers, organics, foods, pharmaceuticals, metals/alloys, ceramics and inorganics as well as the chemical elements.

Database entries can be filtered by a variety of criteria, and measurement curves – even those of different types – can be overlapped for purposes of comparison.

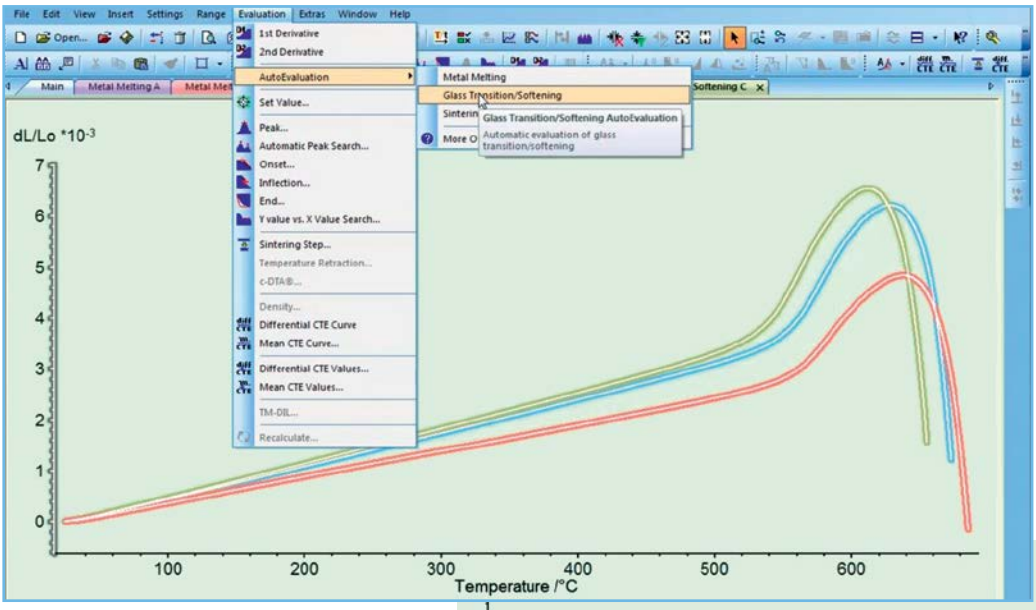
Temperature-Modulated TMA

For temperature-modulated TMA measurements, the modulation amplitude and period can be defined segment by segment. The evaluation software allows for the determination of

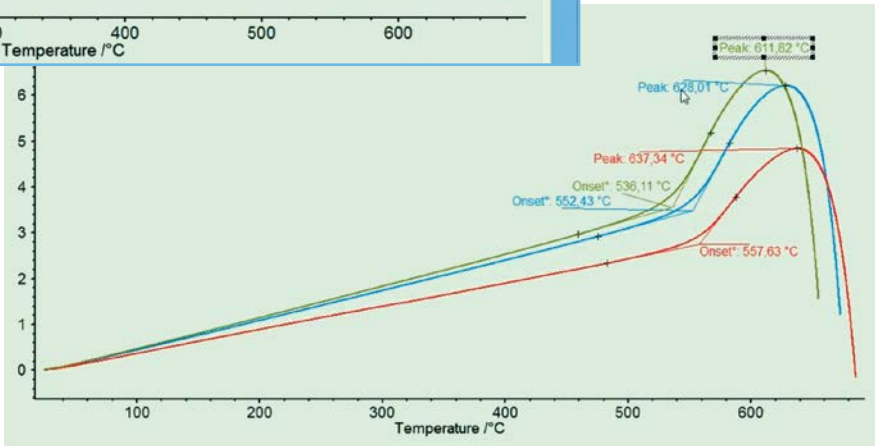
- total TMA
- reversing and non-reversing TMA
- total CTE
- reversing and non-reversing CTE
- amplitude und Phase

with graphic display of the results curve in multi-window technique.

Proteus® also offers the ability to export graphs and print out or export data as ASCII files.



AutoEvaluation on glass transition onsets



AutoEvaluation

AutoEvaluation is an intelligent software functionality exclusively offered by NETZSCH. It is a self-acting evaluatin of thermoanalytical measurement curves that works without using pre-defined macros. This is an immense support and time saver.

AutoEvaluation offers special functions for the evaluation of various materials. When testing Metals, "Metal Melting" will automatically evaluate the onset of melting. "Glass Transition and Softening" displays the onset of glass transition and the peak of softening with just one click. Measuring ceramics, sintering steps will be displayed when sintering of a sample is detected. *AutoEvaluation* is included when you purchase any instrument of the TMA 402 ***F1/F3*** *Hyperion*® range.

Input Assistant for a Fast Start and Method-Based Automatic Evaluation

The *Proteus*® software allows for properties and methods from previously executed measurement files to be applied with a simple mouse click. The evaluation steps for a reference test run can be saved in a method and applied, fully automatically, to a sample measurement after its termination. It is also possible to have the software highlight any results deviating from the selected quality criteria.

Software Options for Advanced Evaluation Steps

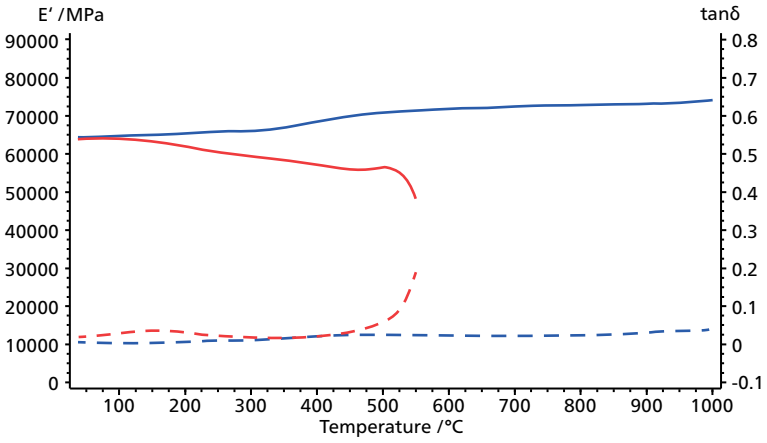
- Expanded evaluation for imported mass spectrometer data from coupling with the QMS 403 D *Aëolos*®
- *Kinetics Neo* for extensive characterization and optimization of sintering processes or curing behavior
- *PeakSeparation* for the separation of overlapping effects

Applications

Comparison of the Visco-Elastic Properties of Fused Silica and Flat Glass

These TMA measurements on fused silica and flat glass were carried out in 3-point bending at a heating rate of 5 K/min between room temperature and 1000°C and 550°C, respectively.

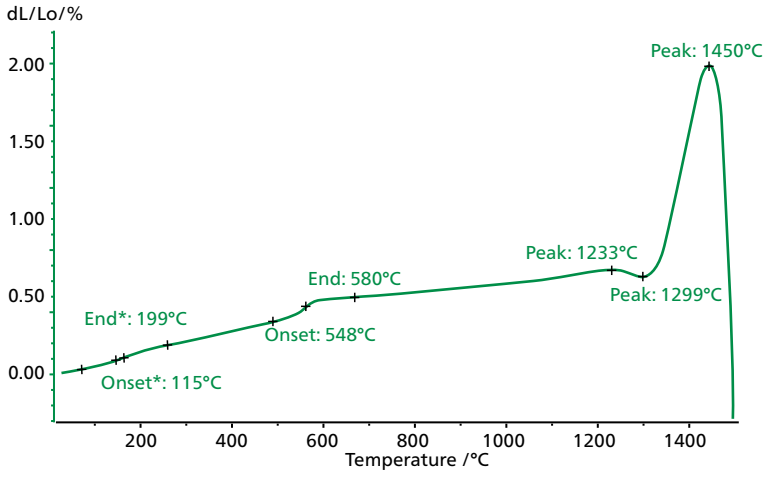
As expected for most materials, the modulus for flat glass decreases with rising temperature until the material's softening point is reached, resulting in a sharp drop in stiffness accompanied by a rising tanδ. In contrast, fused silica exhibits increasing stiffness as temperature rises.



Visco-elastic behavior of two different glass types. Force modulation 0.5 Hz, static force 1.5 N, amplitude 1.45 N, bending distance 20 mm; sample thickness approx. 1 mm, sample width approx. 4.8 mm. Solid lines represent E' modulus; dotted lines, tanδ.

Expansion up to High Temperatures

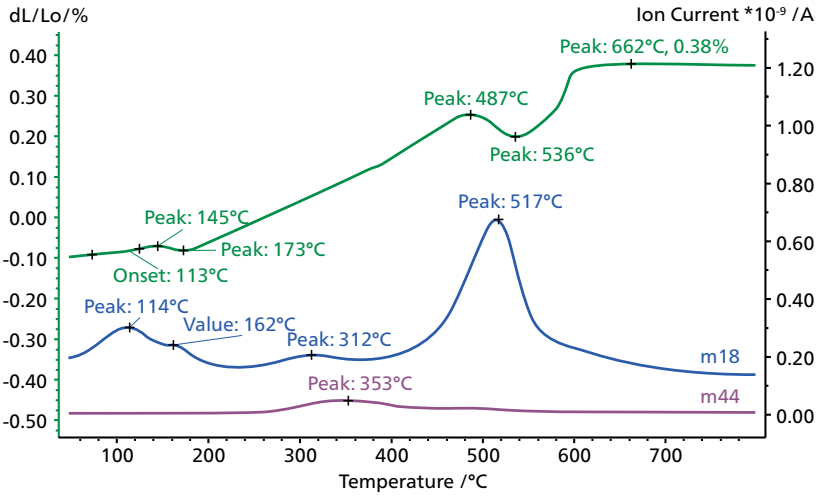
The life span and efficiency of any technical furnace can be greatly improved with appropriate configuration. An important criterion in assessing the materials comprising such furnaces is thermal expansion. Here shown is the thermal behavior of a typical coarse-grained refractory material. At the beginning of the measurement, the α-ß transformation of the tridymite is observed, followed by the α-ß transformation of the free quartz between 548°C and 580°C. After another transformation between 1233°C and 1299° C, the material begins to soften at 1450°C.



TMA measurement on a refractory material between room temperature and 1550°C.

TMA Coupled to Evolved Gas Analysis for Investigation of the Shrinkage Behavior

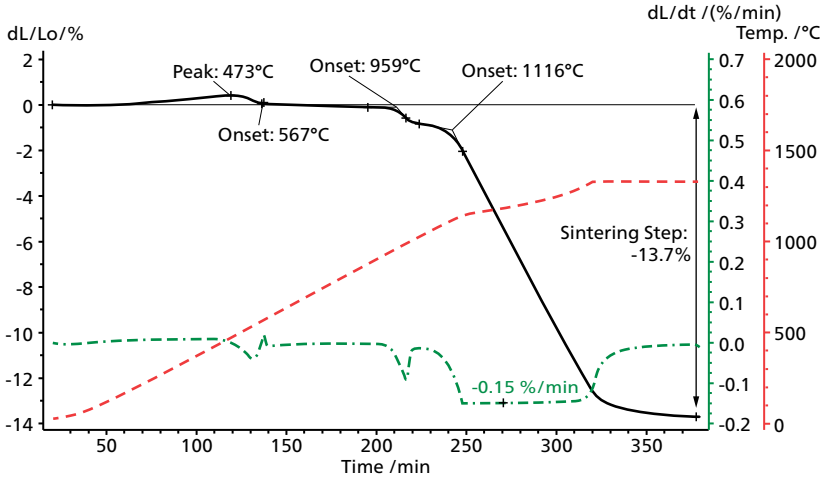
At the beginning of the measurement, the water bound through adsorption and the interlayer water of a clay sample are released (shrinkage of 0.01%; m/z 18). In the range from 300°C up to approx. 450°C, the sample's organic components burn up by releasing water (m/z 18) and CO_2 (m/z 44). Due to the very low organic content, no visible influence on the expansion curve is detectable. Between 487°C and 536°C, dehydroxylation of the sample's clay mineral content takes place. This is associated with a shrinkage of 0.05%.



TMA-MS *Aëolos*® measurement on a clay powder between room temperature and 800°C. The clay powder was placed in a ceramic crucible (see inset picture).

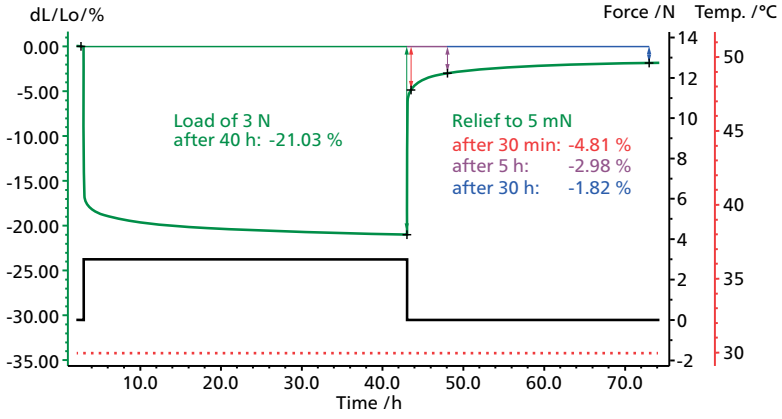
Densification of a Ceramic Green Body by Rate-Controlled Sintering

The sintering of a ceramic green body was here studied using the rate-controlled sintering mode (RCS). The otherwise normal linear temperature profile (red) now changes with the sintering behavior. In the length change curve (black), the dehydroxylation of the kaolinite at 473°C is overlapped by the quartz transition at 567°C (onset). At the onset temperature of 959°C, an additional phase transition takes place, which is confirmed by the peak at 215 min in the 1st derivative of the length change curve (green). At 250 min, sintering starts, with a constant expansion rate of 0.15%/min. The sintering step amounts to 13.7% (black curve).



The RCS measurement in expansion mode (Al_2O_3 sample carrier), SiC furnace between room temperature and 1350°C; sample length approx. 5.5 mm, Ø 6-7 mm, RT -1350°C at a heating rate of 5 K/min followed by an isothermal segment of 60 min; RCS start at 1040°C, start/stop mode, threshold 0.15%.

Testing the Recovery Behavior of Elastomers

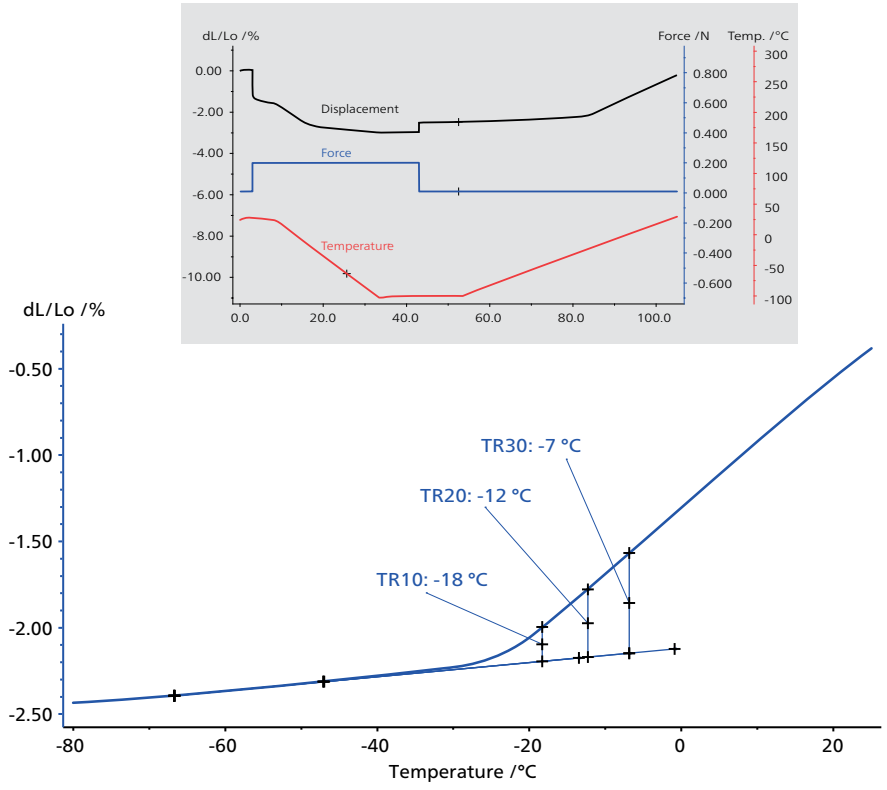


Long-term TMA measurement on an elastomer seal under load

Recovery of a Rubber Seal

The extent to which the elastic properties of a seal remain intact after being subjected to a constant load of longer duration is very important. To test this, an elastomer seal was here loaded with a force of 3 N. Following a 40-hour load time, 21% compression is observed. Then the load is relieved to 5 mN.

After a 30-minute relief period (red value), 95.19% of the initial length was recovered; after a 5-hour relief period (purple value), 97.02%; and after 30 h (blue value), there was only 1.82% that was still not recovered.



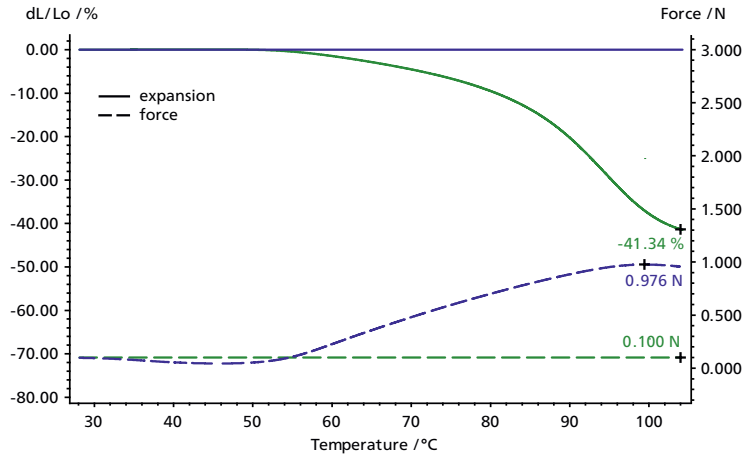
Evaluation of the thermal expansion of the heating segment (main plot); force-temperature program (gray inset).

Temperature Retraction (TR) of Small Samples and O-Rings

The TMA *Proteus*® software allows for determination of the temperature retraction (TR). At room temperature, a small load (0.01 N) is applied to the sample to determine its thickness. The load is then increased and the sample is cooled to approx. 50 K below the expected TR10 point (inset). Thereafter, the load is again relieved and the sample is reheated to room temperature at a rate of 2.5 K/min.

For the evaluation of the TR value, the heating segment is used (main plot). The TR10 value corresponds to a 10% recovery of the sample; the TR20 to a 20% recovery, etc. The TR value is a useful indicator for estimating an elastomer's behavior at low temperatures.

Test on Heat-Shrink Tubing



Displacement control on heat-shrink tubing using a tension sample holder made of fused silica, with displacement kept constant while measuring force. Samples were heated from RT to 120°C, atmosphere N_2, sample size 25 mm (blue) and 10 mm (green).

Heat-shrink tubing, also known as shrink sleeve, is used to repair and insulate wires and cables. After sliding the tubing onto the cable, a heat source is used to make it shrink and create a tight seal. Heat-shrink tubing, by its very nature, is stretchy and changes its shape. A TMA can help gather information about the temperature at which the material starts to shrink, how much it shrinks and with how much force. The plot shows the two samples measured. The first sample starts to shrink at around 60°C with a shrinkage of 40% by the end of the measure-ment (green curves). In the second sample, the displacement was kept constant and the corresponding force measured. A maximum force of 0.98 N (blue curves) was recorded.

TMA 402 ***F1/F3*** *Hyperion®*

Interchangeable, vertical furnaces (located on motorized hoist)	▪ Steel furnace: -150°C to 1000°C ▪ SiC furnace: RT to 1550°C ▪ IC-furnace: -70°C to 450°C ▪ Copper furnace: -150°C to 500°C (possible coupling to humidity generator) ▪ Water-vapor furnace: RT to 1250°C (for measurements under steam by coupling to water-vapor generator or to humidity generator)
Heating/cooling rates	0.001 K/min to 50 K/min
Cooling systems	▪ For steel and copper furnace: ▪ Liquid nitrogen cooling (optional with 60-liter Dewar; convenient refill system) ▪ Vortex tube (based on compressed air) ▪ Intracooler for IC-furnace ▪ Forced air for SiC-furnace
Measurement modes	Expansion, penetration, 3-point bending, tension
Measuring ranges/ Δl resolution	▪ 500 m (± 250 m) / 0.125 nm ▪ 5000 µm (± 2500 µm) / 1.25 nm
Force and displacement	Simultaneous measurement of force and displacement signal
Force range (load at sample)	0.001 N to 3N (***F3***) /4 N (***F1***) in steps of 0.02 mN without using additional weights
Force resolution	< 0.01 mN
Modulated force	▪ 0.0003 Hz to 1 Hz; customizable frequencies ▪ Wave forms: square, sinusoidal, triangular, steps, ramps, single pulses
Interchangeable sample holder systems	▪ Fused silica: up to 1100°C ▪ Alumina: up to 1550°C
Special sample containers	For tests on pastes, powders, liquids, waxes, molten metals, immersion
Sample dimensions	▪ Length: 30 mm max.; alumina sample holder Ø 10 mm max., fused silica sample holder Ø 12 mm / 8 mm; ▪ Automatic sample length determination (precision: 0.01 mm)
Atmospheres	Software-controlled, inert, oxidizing, reducing, vacuum

The NETZSCH Group is an owner-managed, international technology company with headquarters in Germany. The Business Units Analyzing & Testing, Grinding & Dispersing and Pumps & Systems represent customized solutions at the highest level. More than 3,800 employees in 36 countries and a worldwide sales and service network ensure customer proximity and competent service.

Our performance standards are high. We promise our customers Proven Excellence – exceptional performance in everything we do, proven time and again since 1873.

When it comes to Thermal Analysis, Calorimetry (adiabatic & reaction), the determination of Thermophysical Properties, Rheology and Fire Testing, NETZSCH has it covered. Our 50 years of applications experience, broad state-of-the-art product line and comprehensive service offerings ensure that our solutions will not only meet your every requirement but also exceed your every expectation.

Proven Excellence.

NETZSCH-Gerätebau GmbH
Wittelsbacherstraße 42
95100 Selb
Germany
Tel.: +49 9287 881-0
Fax: +49 9287 881 505
at@netzsch.com

NETZSCH®

www.netzsch.com

NGB · TMA 402 ***F1/F3*** *Hyperion®* · EN · 0621 · NWS · Technical specifications are subject to change.